

## PATENT ABSTRACTS OF JAPAN

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## (54) PREPARATION PROCESS OF NORBORNENE-BASED RING-OPENING POLYMER HYDRIDE

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a preparation process of crystalline norbornene-based ring-opening polymer and its hydride and to provide a catalyst compound for the process and its preparation process.

SOLUTION: (1) Using a polymerization catalyst comprising a reaction product between a halogenide or oxyhalogenide of a specific transition metal and an aromatic mono-ol or an aromatic mono-oxide, and an organic metal reducing agent, a norbornene-based monomer is polymerized by a metathesis ring-opening polymerization. Then the polymer is hydrogenated. (2) Using a polymerization catalyst comprising a reaction product between a halogenide or oxyhalogenide of a specific transition metal and an aromatic di-ol or an aromatic di-oxide, and an organic metal reducing agent, a norbornene-based monomer is polymerized by a metathesis ring-opening polymerization. Then the polymer is hydrogenated.

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CLAIMS

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[Claim(s)]

[Claim 1]A manufacturing method of a crystalline norbornene system ring-opening-polymerization object hydride which hydrogenates not less than 50% of carbon-carbon double bonds which exist in a main chain of this obtained polymer after carrying out the ring opening methathesis of the norbornene system monomer under an existence of a polymerization catalyst characterized by comprising the following under hydrogenation catalyst existence.

Reactant (I) with the aromatic monooxars or aromatic monooxide (b) which has a halogenide, a oxy halogenide or a dioxy halogenide (a), and a substituent of the 4-6th group transition metals of the periodic table.

Organic metal reducing agent (II).

[Claim 2]A manufacturing method of a crystalline norbornene system ring-opening-polymerization object which carries out the ring opening methathesis of the norbornene system monomer under existence of a polymerization catalyst characterized by comprising the following. Reactant (III) of a halogenide of the 4-6th group transition metals of the periodic table, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c).

Organic metal reducing agent (II).

[Claim 3]A manufacturing method of a crystalline norbornene system ring-opening-polymerization object which carries out the ring opening methathesis of the norbornene system monomer under existence of a polymerization catalyst which consists of the 4-6th group transition metal oxy ghost of the periodic table or halogenide (IV) which has an aromatic dioxy group as a ligand, and organic metal reducing agent (II).

[Claim 4]A manufacturing method of a crystalline norbornene system ring-opening-polymerization object hydride which hydrogenates not less than 50% of carbon-carbon double bonds which exist in a main chain of a crystalline norbornene system ring-opening-polymerization object acquired by a method according to claim 2 or 3 under hydrogenation catalyst existence.

[Claim 5]A polymerization catalyst containing the 4th fellows of the periodic table who have an aromatic dioxy group as a ligand - 6 group-transition-metal oxy compound, or halogenide (IV).

[Claim 6]How to manufacture a polymerization catalyst which makes a halogenide, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c) of the 4-6th group transition metals of the periodic table react, and contains the oxy compound according to claim 5 or halogenide (IV).

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the manufacturing method of the norbornene system ring-opening-polymerization object which has crystallinity, or this ring-opening-polymerization object hydride.

[0002]

[Description of the Prior Art]The ring opening metathesis of the norbornene system monomer using the transition metal compound of the 4-9th fellows of the periodic table is well known from the former.

Transition metal compounds, such as Nb, Ta, Re, Zr, Ti, Ru, Os, Ir, etc. besides W of the 6th fellows of the periodic table or Mo, are used as a ring opening polymerization catalyst.

The polymerization catalyst which consists of the halogenide or the oxy halogenide, hydrogenation trio luanot tin, and boron trihalide of W which have a phenoxy group as a ligand is used, The resultant and co-catalyst of an imide transition metal compound and biphenol which carry out ring opening polymerization of the dicyclopentadiene are used, [ of a method (U. S.PAT.NO.5218065) or the 5-8th fellows of the periodic table ] The method (U.

S.PAT.NO.5405924) of carrying out metathesis polymerization of the cyclic olefin, such as a dicyclopentadiene, is reported. These are only indicating having carried out ring opening polymerization. The Ziegler type polymerization catalyst using the halogenide, oxy halogenide, and organic metal reducing agent of W or Mo is known widely. For example, the polymerization catalyst which consists of organic tin, such as halogenides, such as  $WCl_6$  and  $MoCl_5$ ,

tetraphenyltin, and tetra(n-butyl) tin, A oxy halogenide and triethylaluminums, such as  $WOCl_4$  and  $MoOCl_4$ , A diethylaluminium chloride, the polymerization catalyst etc. which consist of organic aluminium, such as ethyl aluminum dichloride, are known well ( ' — the volume OlefinMetathesis and Metathesis Polymerization'KJ.Ivan and on J.C.Mol.) 1997, ACADEMIC PRESS, TOKYO, etc. However, the ring-opening-polymerization object of the norbornene system monomer which polymerized in these Ziegler type polymerization catalysts, or its hydride is amorphous, and does not have the melting point. When this polymer was used for various uses, there was the time when mechanical strength, heat resistance, solvent resistance, etc. are insufficient. Therefore, development of the polymerization catalyst used for the method and it which have the melting point in order to solve these problems, namely, manufacture the norbornene system ring-opening-polymerization object which has crystallinity, or its hydride was desired.

[0003]

[Problem(s) to be Solved by the Invention]The purpose of this invention is to provide the catalyst used for the manufacturing method of a crystalline norbornene system ring-opening-polymerization object and its hydride, and it, and its manufacturing method.

[0004]

[Means for Solving the Problem]In order that this invention persons may solve an aforementioned problem, as a result of inquiring wholeheartedly, a reactant with a halogenide of a specific transition metal, a oxy halogenide or a dioxy halogenide, an aromatic monoar, or

aromatic monooxide, A polymer hydride which has crystallinity when the ring opening methathesis of the norbornene system monomer is carried out and it hydrogenates continuously using a polymerization catalyst which consists of an organic metal reducing agent is obtained, A reactant of a halogenide of a specific transition metal, a oxy halogenide or a dioxy halogenide, aromaticdiol, or aromaticdioxide, If the ring opening methathesis of the norbornene system monomer is carried out using a polymerization catalyst which consists of an organic metal reducing agent and it hydrogenates if needed, it will find out that a polymer and/or a hydride which have crystallinity are obtained, and based on this knowledge, it came to complete this invention. According to this invention in this way [0005](1) Reactant (I) with the aromatic monooxars or aromatic monooxide (b) which has a halogenide, a oxy halogenide or a dioxy halogenide (a), and a substituent of the 4-6th group transition metals of the periodic table, After carrying out the ring opening methathesis of the norbornene system monomer under existence of a polymerization catalyst which consists of organic metal reducing agent (II), A manufacturing method of a crystalline norbornene system ring-opening-polymerization object hydride which hydrogenates not less than 50% of carbon-carbon double bonds which exist in a main chain of this obtained polymer under hydrogenation catalyst existence, (2) Reactant (III) of a halogenide of the 4-6th group transition metals of the periodic table, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c), A manufacturing method of a crystalline norbornene system ring-opening-polymerization object which carries out the ring opening methathesis of the norbornene system monomer under existence of a polymerization catalyst which consists of organic metal reducing agent (II), (3) A manufacturing method of a crystalline norbornene system ring-opening-polymerization object which carries out the ring opening methathesis of the norbornene system monomer under existence of a polymerization catalyst which consists of the 4th fellows of the periodic table who have an aromatic dioxy group as a ligand - the 6th group transition metal oxy compound or halogenide (IV), and organic metal reducing agent (II). A manufacturing method of a crystalline norbornene system ring-opening-polymerization object hydride which hydrogenates not less than 50% of carbon-carbon double bonds which exist in a main chain of this ring-opening-polymerization object acquired by a method (4), (2), or given in (3) under hydrogenation catalyst existence, (5) A polymerization catalyst containing the 4th fellows of the periodic table who have an aromatic dioxy group as a ligand - the 6th group transition metal oxy compound, or a halogenide, (6) A halogenide, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c) of the 4-6th group transition metals of the periodic table is made to react, and a method of manufacturing a polymerization catalyst given in (5) is provided.

[0006]

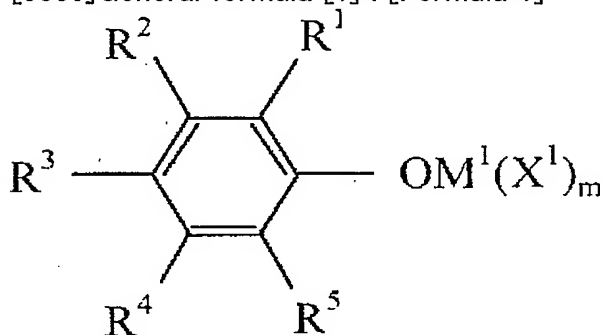
[Embodiment of the Invention]In the manufacturing method of this invention, the ring opening methathesis of the norbornene system monomer is carried out using the polymerization catalyst which consists of reactant (I), (III), or compound (IV) and organic metal reducing agent (II), and a hydrogenation reaction is carried out further if needed. Reactant (I) of this invention The halogenide of the 4-6th group transition metals of the periodic table, A reactant with the aromatic monooxars or aromatic monooxide (b) which has a oxy halogenide or a dioxy halogenide (a), and a substituent, and reactant (III), The reactant of the halogenide of the 4-6th group transition metals of the periodic table, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c), Compound (IV) is the 4th fellows of the periodic table who have an aromatic dioxy group as a ligand - the 6th group transition metal oxy compound, or a halogenide.

[0007]the halogenide of the 4-6th group transition metals of the periodic table, a oxy halogenide, or a dioxy halogenide (a) -- (--- it is hereafter called "a compound (a)".) -- as the 4th fellows of the periodic table - the 6th group transition metal to constitute, Ti, Zr, V, Nb, Ta, Mo, W, etc. can be mentioned. Mo and W have highly preferred polymerization activity also in it. As a halogenide of this transition metal,  $TiCl_4$ ,  $ZrCl_4$ ,  $VCl_5$ ,  $NbCl_5$ ,  $TaCl_5$ ,  $MoCl_5$ ,  $WCl_6$ ,  $TiBr_4$ ,  $ZrBr_4$ ,  $VBr_5$ ,  $NbBr_5$ ,  $TaBr_5$ ,  $MoBr_5$ ,  $WBr_6$ ,  $TiF_4$ ,  $ZrF_4$ ,  $VF_5$ ,  $NbF_5$ ,  $TaF_5$ ,  $MoF_5$ ,  $WF_6$ ,  $TiI_4$ ,  $ZrI_4$ ,  $VI_5$ ,  $NbI_5$ ,  $TaI_5$ ,  $MoI_5$ ,  $WI_6$ , etc. can be mentioned. As a oxy halogenide of the 4-6th group transition metals of the periodic table,  $VOCl_3$ ,  $MoOCl_4$ ,  $WOCl_4$ ,  $VOBr_3$ ,  $MoOBr_4$ ,  $WOBr_4$ ,  $VOF_3$ ,  $MoOF_4$ ,  $WOF_4$ ,  $VOI_3$ ,  $MoOI_4$ ,  $WOI_4$ ,

etc. can be mentioned. As a dioxy halogenide of the 4-6th group transition metals of the periodic table,  $\text{MoO}_2\text{Cl}_2$ ,  $\text{WO}_2\text{Cl}_2$ ,  $\text{MoO}_2\text{Br}_2$ ,  $\text{WO}_2\text{Br}_2$ ,  $\text{MoO}_2\text{F}_2$ ,  $\text{WO}_2\text{F}_2$ ,  $\text{MoO}_2\text{I}_2$ ,  $\text{WO}_2\text{I}_2$ , etc. can be mentioned.

[0008]the aromatic monooars which have a substituent used for this invention, or aromatic monooxide (b) -- (--- it is hereafter called "a compound (b)".) -- it has one hydroxyl group and they are aromatic compounds which have a substituent, or its metal salt (except for a hydroxyl group) further. A bulky substituent is preferred although a substituent in particular is not limited. Specifically, a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group is mentioned. It is preferred to have a substituent to carbon of the next door of the carbon which the oxide group has combined especially. And this substituent is so preferred that it is bulky, for example, its halo alkyl groups, such as the 3rd class alkyl groups, such as the 2nd class alkyl groups, such as an iso-propyl group, and t-butyl group, a phenyl group or a substituted phenyl group, and a trifluoromethyl group, are preferred. It is a general formula [1] as a constructional example of a compound (b).

[0009]General formula [1] : [Formula 1]



( $R^1$  and  $R^5$  show a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group independently among a formula, respectively.) A hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group may be shown independently, respectively, it may combine with each other, and  $R^2 - R^4$  may form a ring structure. The metal atom in which  $M^1$  is chosen from a hydrogen atom or alkaline metals (Li, Na, K, etc.), alkaline-earth metals (Mg, Ba, etc.), and aluminum.  $m$  is decided by the integer of 0-2 with the valence of the element of  $M^1$ .  $X^1$  is a halogen atom. What is expressed is mentioned.

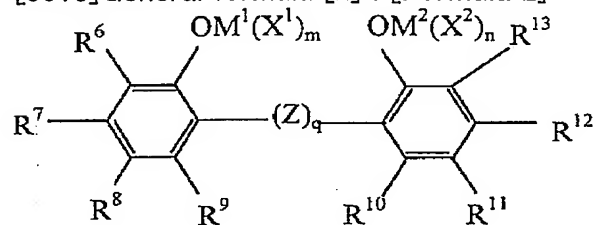
[0010]When these examples are given, 2,6-dimethylphenol, 2,6-diethylphenol, 2,6-JI (iso-propyl) phenol, 2,6-JI (t-butyl) phenol, 2,6-JI (t-butyl)-4-methyl phenol, 2,6-diphenylphenol, Phenols, such as 2,6-JI (trifluoromethyl) phenol; 2,6-JI (iso-propyl) phenoxysodium, 2,6-JI (t-butyl) phenoxylithium, 2,6-JI (t-butyl)-4-methylphenoxy potassium, Phenoxide; 2,6-JI (iso-propyl) phenoxymagnesiumbromide, such as 2,6-diphenylphenoxylithium and 2,6-JI (trifluoromethyl) phenoxylithium, 2,6-JI (t-butyl) phenoxymagnesiumchloride, 2,6-JI (t-butyl)-4-methylphenoxy aluminumdichloride, Phenoxide, such as 2,6-diphenylphenoxymagnesiumbromide and 2,6-JI (trifluoromethyl) phenoxymagnesiumbromide, can be mentioned.

[0011]The naphthols or naphtho KISHIDO which an aromatic ring combined with phenols or phenoxide further, anthra SENORU or anthra SENOKISHIDO, etc. can also be mentioned. When these examples are given, 1,3-JI (iso-propyl)-2-naphthol, 1,3-JI (t-butyl)-2-naphthoxy lithium, 2-(iso-propyl)-1-naphthol, 2-phenyl-1-naphthol, 2-phenyl-1-naphthoxy lithium, 1,3-JI (t-butyl)-2-naphthoxy aluminumdichloride, Naphthols or naphtho KISHIDO, such as 2-phenyl-1-naphthoxy magnesiumbromide; anthra SENORU or anthra SENOKISHIDO, such as 9-anthra SENORU and 2-methyl-1-anthra SENORU, can be mentioned.

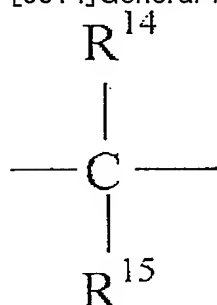
[0012]the aromaticdiol used for this invention, or aromaticdioxide (c) -- (--- it is hereafter called "a compound (c)".) -- they are aromatic compounds which have two or more hydroxyl groups, or

its metal salt. As for a compound (c), what has a substituent further is preferred. As for a substituent, what is combined with carbon of a next door of carbon combined with a oxy group is preferred. Especially a thing that has a bulky substient is preferred, and what was shown with a compound (b), and same thing are mentioned as a bulky substient. As a constructional example of a compound (c), what is expressed with a general formula [2] and [3] is preferred.

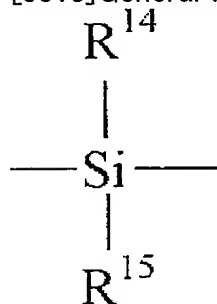
[0013]General formula [2] : [Formula 2]



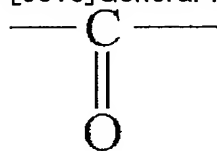
[0014]General formula [3] : [Formula 3]



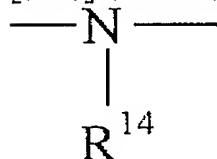
[0015]General formula [4] : [Formula 4]



[0016]General formula [5] : [Formula 5]



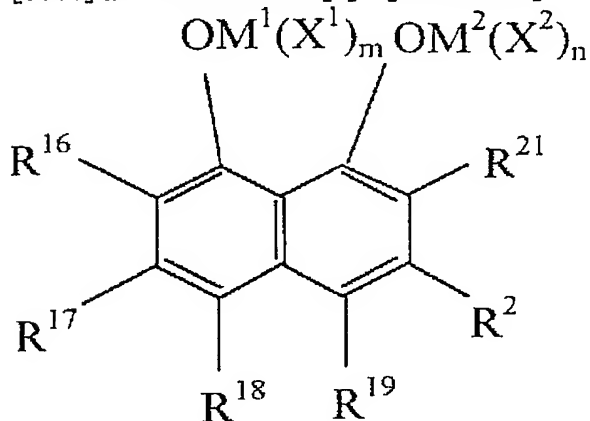
[0017]General formula [6] [Formula 6]



(Among a formula,  $R^6 - R^{13}$  are a hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group independently, and it may combine with each other and they may form a ring structure, respectively.) Z is chosen from a general formula [3], a general formula [4], a general formula [5], a general formula [6], an oxygen atom, and a sulfur atom. Here,  $R^{14}$  and  $R^{15}$

express a hydrogen atom or hydrocarbon of the carbon numbers 1-6. q is 0 or 1. The metal atom in which  $M^1$  and  $M^2$  are independently chosen from a hydrogen atom or alkaline metals (Li, Na, K, etc.), alkaline-earth metals (Mg, Ca, Ba, etc.), and aluminum, respectively. X is decided with a halogen atom and m and n are decided by the integer of 0-2 with the valence of the element of  $M^1$  and  $M^2$ .

[0018]General formula [7] : [Formula 7]



(Among a formula,  $R^{16} - R^{21}$  are a hydrogen atom, a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group independently, and it may combine with each other and they may form a ring structure, respectively.) The metal atom in which  $M^1$  and  $M^2$  are independently chosen from a hydrogen atom or alkaline metals (Li, Na, K, etc.), alkaline-earth metals (Mg, Ca, Ba, etc.), and aluminum, respectively. X is decided with a halogen atom and m and n are decided by the integer of 0-2 with the valence of the element of  $M^1$  and  $M^2$ .

0, i.e., biphenol, or biphenoxy has most preferred q in a general formula [2].

[0019]When q in a general formula [2] gives the example of what is 0, 2 and 2'-biphenol, 3,3'-dimethyl- 2,2'-biphenol, the 3,3'-diethyl- 2, 2'-biphenol, 3,3'-JI (iso-propyl)-2,2'-biphenol, 3,3'-JI (t-butyl)-2, and 2'-biphenol, 3,3'-JI (t-butyl)-5 and 5',6,6' - tetramethyl 2 and 2'-biphenol, Biphenol, such as 3,3'-Gia Daman \*\*\*\*- 5,5',6,6'-tetramethyl 2,2'-biphenol; 2,2'-biphenoxy lithium, 3,3'-dimethyl- 2,2'-biphenoxy sodium, 3,3'-diethyl- 2,2'-biphenoxy potassium, 3,3'-JI (iso-propyl)-2,2'-biphenoxy lithium, 3,3',5,5'-tetra (t-butyl)-2,2'-biphenoxy sodium, 3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy lithium, 3,3'-Gia Daman \*\*\*\*- 5,5',6,6'-tetramethyl 2,2'-biphenoxy potassium, 2,2'-biphenoxy magnesiumbromide, 3,3'-diethyl- 2,2'-biphenoxy magnesiumchloride, 3,3'-JI (iso-propyl)-2,2'-biphenoxy aluminumdichloride, 3,3'-JI (t-butyl)-2,2'-biphenoxy magnesiumchloride, 3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy aluminumdibromide, BIFENOKISHIDO, such as 3,3'-Gia Daman \*\*\*\*- 5,5',6,6'-tetramethyl 2,2'-biphenoxy magnesiumbromide, can be mentioned.

[0020]The binaphthols or BINAFTOKISHIDO etc. which an aromatic ring combined with biphenol or BIFENOKISHIDO further can also be mentioned. As these examples, 1,1'-binaphthyl 2,2'-diol, 3,3'-dimethyl- 1,1'-binaphthyl 2,2'-dioxyllithium, 3,3'-diethyl- 1,1'-binaphthyl 2,2'-dioxypotassium, 3,3'-JI (iso-propyl)-1,1'-binaphthyl 2,2'-dioxymagnesiumbromide, 3,3'-JI (t-butyl)-1,1'-binaphthyl 2,2'-diol, 3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxyllithium, 3,3'-Gia Daman \*\*\*\*- 1,1'-binaphthyl 2,2'-dioxyaluminumdichloride, etc. can be mentioned.

[0021]When q in a general formula [2] gives an example of what is 1, 2,2'-methylenebis (4-chlorophenol), 2,2'-methylenebis (6-t-butyl-4-methyl phenol), 2,2'-methylenebis (6-t-butyl-4-ethylphenol), 2,2'-methylenebis (3,4,6-trichlorophenol), the 3,3'-JI (t-butyl)-2,2'-dihydroxy- 1, 1'-diphenyl ether, The 3,3'-JI (t-butyl)-2,2'-dihydroxy- 1, 1'-diphenylthioether, 1,8-dihydroxyanthraquinone, or these metal salt can be mentioned.

[0022]if an example of the naphthodiol shown by a general formula [7] is given -- 1,8-naphthodiol, 2,7-diphenyl-1,8-naphthodiol, 2,7-dimethyl- 1,8-naphthodiol, and 2,7-JI (t-butyl)-

1,8-naphthodiol \*\*\*\*\* -- things are made.

[0023]Reactant (I) used for this invention is obtained by mixing a compound (b) with a compound (a). Reactant (III) is obtained by mixing a compound (a) and a compound (c). A compound (a), a compound (b), or a compound (c) is usually mixed, after dissolving or distributing to an organic solvent. An organic solvent to be used will not be limited in particular, if a compound (a), a compound (b), or a compound (c) is dissolved or distributed and a reaction is not influenced.

[0024]As such an organic solvent, they are aromatic hydrocarbon system solvents, such as benzene, toluene, and xylene, concretely; Dichloromethane, Halogen system aliphatic hydrocarbon system solvents, such as chloroform and 1,2-dichloroethane; Chlorobenzene, Halogen system aromatic hydrocarbon system solvents, such as dichlorobenzene; Nitromethane, Nitrogen-containing hydrocarbon system solvents, such as nitrobenzene and acetonitrile; Diethylether, Ether system solvents, such as a tetrahydrofuran; Aromatic ether system solvents, such as an anisole and phenetol; Pentane, Aliphatic hydrocarbon system solvents, such as hexane and heptane; alicycle fellows hydrocarbon system solvents, such as cyclohexane, a methylcyclohexane, decahydronaphthalene, bicycloheptane, tricyclodecane one, and cyclooctane, etc. can be used. Also in these solvents, an aromatic hydrocarbon system solvent, a halogen system aromatic hydrocarbon system solvent, an ether system solvent, or an aromatic ether system solvent is excellent in the solubility of a compound (a), a compound (b), or a compound (c), and since there is little influence of a polymerization reaction and a hydrogenation reaction on subsequent, it is desirable. Concentration of a compound (a) in a solution containing a compound (a), a compound (b), or a compound (c), a compound (b), or a compound (c) can be chosen arbitrarily.

[0025]Mixing may be performed under rare gas, such as argon, or a nitrogen gas atmosphere, and a solution which contains a compound (b) or a compound (c) in a solution containing a compound (a) may be added, and the contrary may be sufficient, and both may be simultaneously added to another container and it may mix. As for a rate over a compound (a) of a compound (b) or a compound (c), one to 10 times are preferred at a mole ratio, it is more preferred, and is preferred. [ of especially one to 5 times ] [ of one to 8 times ] When there are too few rates over a compound (a) of a compound (b) or a compound (c), an unreacted compound (a) may remain and a polymerization may be checked. When too large, an unreacted compound (b) or a compound (c) influences a polymerization, and a side reaction may be caused. Although reaction temperature in particular is not limited, generally, it is performed between -100 °C - 100 °C. When too high [ when temperature is too low, advance of a reaction is too slow, and ], a side reaction may occur, or output may decompose. A range with preferred reaction temperature is -80 °C - 80 °C, and a still more desirable range is -70 °C - 70 °C. It is preferred to make it react, ranking second at low temperature 0 °C or less, and raising [ mix, ] temperature to near a room temperature gradually. Reaction time will not be limited in particular, if it is during -1 week for 1 minute.

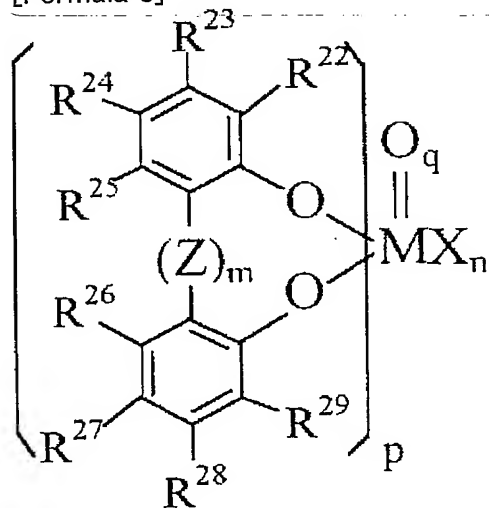
[0026]An organic solvent insoluble [ (III) / resultant (I) or ] in reaction mixture as it is, (I), or (III). Reaction mixture can be added to (for example, saturated hydrocarbon system solvents, such as pentane), and what deposited (I) or (III), or distilled off and collected solvents used for a reaction can be used as a polymerization catalyst.

[0027]The main ingredients of reactant (I) are the 4-6th group transition metal compound of the periodic table which has as a ligand an aromatic monooxy group which has a substituent. To carbon of a next door of carbon which a oxy group has combined especially, a bulky substituent, For example, the 3rd class alkyl groups, such as the 2nd class alkyl groups, such as an iso-propyl group, and t-butyl group, Since what has halo alkyl groups, such as a phenyl group or a substituted phenyl group, and a trifluoromethyl group, etc. can perform a high polymerization reaction of tacticity and can obtain a crystalline norbornene system ring-opening-polymerization object hydride, it is preferred. The main ingredients of reactant (III) are the 4-6th group transition metal compound of the periodic table which has an aromatic dioxy group as a ligand. Since tacticity is improved more by making into a ligand an aromatic dioxy group which is high 2 seat ligand of solid restrictiveness, a high crystalline norbornene system ring-opening-polymerization object and its hydride can be obtained.



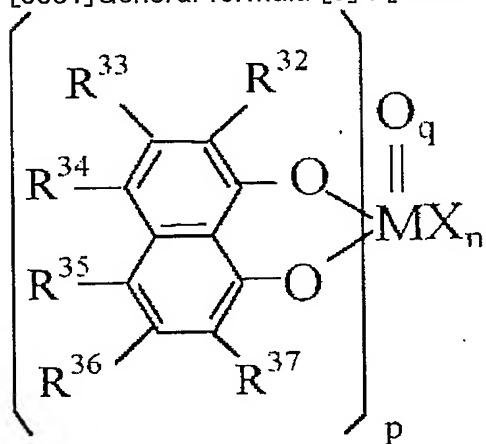
[0028] Resultant (I) or (III) can isolate with the above-mentioned separation method. When it isolates, structure of an obtained compound can be identified by a  $^1\text{H}$ -NMR spectrum or ultimate analysis.

[0029] The 4th fellows of the periodic table who have as a ligand an aromatic dioxy group used for this invention - 6 group-transition-metal oxy compound, or halogenide (IV) is the main ingredients of reactant (III). For example, a general formula [8] or [9] [0030] General formula [8] : [Formula 8]



the inside of a formula, and M -- the 4-6th group transition metal atoms of the periodic table, and X -- a halogen atom,  $\text{R}^{22} - \text{R}^{29}$  -- respectively -- independent -- a hydrogen atom. It is a halogen atom, an alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group, and it may combine with each other and a ring structure may be formed. Z is chosen from a general formula [3], a general formula [4], a general formula [5], a general formula [6], an oxygen atom, and a sulfur atom. Here,  $\text{R}^{30}$  and  $\text{R}^{31}$  express a hydrogen atom or hydrocarbon of the carbon numbers 1-6 independently, respectively. As for 0 or 1, and n, 1 or 2, and q of 0-4p are [ m ] 0-2, and  $n+p+q$  is decided by a valence of M element.

[0031] General formula [9] : [Formula 9]



the inside of a formula, and M -- the 4-6th group transition metal atoms of the periodic table, and X -- a halogen atom,  $\text{R}^{32} - \text{R}^{37}$  -- respectively -- independent -- a hydrogen atom. It is a halogen atom, the alkyl group of the carbon numbers 1-12, an aryl group, an alkoxy group, an aryloxy group, a halo alkyl group, a halo aryl group, or a cyano group, and it may combine with each other and a ring structure may be formed. As for 0-4p, 1 or 2, and q of n are 0-2, and  $n+p+q$  is decided by the valence of M element. It is expressed.

[0032] Especially, a metal oxy compound or a halogenide whose central metal is Mo or W is the most preferred in respect of polymerization activity. As an example of this metal complex, screw {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} oxymolybdenum (VI), {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} oxymolybdenum (VI) dichloride, Screw {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} oxymolybdenum (VI), {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} oxymolybdenum (VI) dichloride, Screw {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} oxytungsten (VI), {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} oxytungsten (VI) dichloride, Screw {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} oxytungsten (VI), {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} oxytungsten (VI) dichloride, Screw {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} tungsten (VI) dichloride, {3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy} tungsten (VI) tetrachloride, Screw {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} tungsten (VI) dichloride, {3,3'-diphenyl-1,1'-binaphthyl 2,2'-dioxy} tungsten (VI) tetrachloride, etc. can be mentioned.

[0033] These compounds are obtained by making a halogenide, a oxy halogenide or a dioxy halogenide (a), aromaticdiol, or aromaticdioxide (c) of the 4-6th group transition metals of the periodic table react, and dissociating. The same method as a case where reactant (III) is generated can be used for reaction conditions.

[0034] In this invention, the 4th fellows of the periodic table who have above resultant (I), (III), or an aromatic dioxy group as a ligand - 6 group-transition-metal oxy compound, or halogenide (IV) combines with organic metal reducing agent (II) -- high -- it becomes an activity polymerization catalyst.

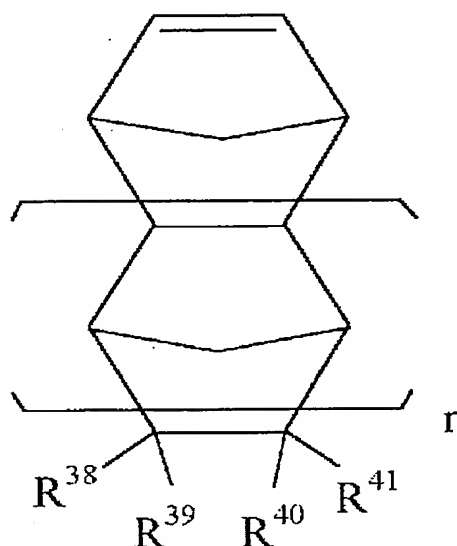
[0035] The organic metal reducing agent can mention an organic metallic compound of periodic table the 1st, 2, 12, 13, and 14 fellows who have a hydrocarbon group of the carbon numbers 1-20. Especially, organic lithium, organic magnesium, organic zinc, organic aluminium, or organic tin is preferred, and organic lithium, organic aluminium, or especially organic tin is preferred. As organic lithium, n-butyl lithium, methyl lithium, phenyllithium, neopentyl lithium, neo fill lithium, etc. can be mentioned. As organic magnesium, butylethylmagnesium, butyloctylmagnesium, Dihexylmagnesium, ethylmagnesiumchloride, n-butylmagnesiumchloride, allylmagnesiumbromide, neopentyl magnesiumchloride, neo fill magnesiumchloride, etc. can be mentioned. Dimethyl zinc, diethylzinc, diphenylzinc, etc. can be mentioned as organic zinc. As organic aluminium, trimethylaluminum, triethylaluminum, triisobutylaluminum, a diethylaluminium chloride, ethylaluminium sesquichloride, ethyl aluminum dichloride, etc. can be mentioned. Tetramethyltin, tetra(n-butyl) tin, tetraphenyltin, etc. can be mentioned as organic tin.

[0036] As opposed to a central metal of the 4-6th group transition metal oxy compound of the periodic table, or halogenide (IV) in which quantity of an organic metal reducing agent has reactant (I), (III), or an aromatic dioxy group as a ligand, 0.1 to 100 times are preferred at a mole ratio, 0.2 to 50 times are more preferred, and especially 0.5 to 20 times are preferred.

Polymerization activity of an addition does not improve in 0.1 or less time, but a side reaction occurs easily that they are 100 or more times.

[0037] A monomer used in a manufacturing method of this invention is a norbornene system monomer, and, specifically, is a general formula [10].

[0038] General formula [10] : [Formula 10]



(Among a formula, the substituent containing the hydrocarbon group of a hydrogen atom and the carbon numbers 1-20 or a halogen atom, a silicon atom, an oxygen atom, or a nitrogen atom may be shown,  $R^{38}$  and  $R^{41}$  may join together, and  $R^{38} - R^{41}$  may form a ring.)  $r$  is an integer of 0-2. The norbornene whose  $r$  it is shown and is 0. The norbornene derivative in which  $R^{38}$  and  $R^{41}$  join together by 0, and  $r$  has a ring structure in addition to a norbornene ring, the tetracyclododecene whose  $r$  is 1, and the hexacycloheptadecene whose  $r$  is 2 can be mentioned. Especially, since the norbornene derivative or tetracyclododecene which has a ring structure in addition to norbornene and a norbornene ring tends to obtain a crystalline polymer hydride, it is preferred, and especially the norbornene derivative that has a ring structure in addition to norbornene or a norbornene ring is preferred.

[0039] Any monomer can be used although  $r$  of a general formula [10] can classify as follows the norbornene which is 0 according to a substituent of  $R^{38} - R^{41}$ . As an example of norbornene, norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-butyl norbornene, 5-hexyl norbornene, Norbornene;5-ethylidene norbornene which has no replacing or alkyl groups, such as 5-decyl norbornene, 5-cyclohexyl norbornene, and 5-cyclopentyl norbornene, Norbornene which has aromatic rings, such as norbornene;5-phenyl norbornene which has alkenyl groups, such as 5-vinyl norbornene, 5-propenyl norbornene, 5-cyclohexenyl norbornene, and 5-cyclopentenyl norbornene;

[0040] 5-carbomethoxy norbornene, 5-ethoxycarbonyl norbornene, 5-methyl-5-carbomethoxy norbornene, 5-methyl-5-ethoxycarbonyl norbornene, Knoll \*\*\*\*\*- 2-methylpropionate, Knoll \*\*\*\*\*- 2-methylocta NEITO, A norbornene 5,6-dicarboxylic anhydride, 5-hydroxymethyl norbornene, 5,6-JI (hydroxymethyl) norbornene, 5,5-JI (hydroxymethyl) norbornene, 5-hydroxy-*i*-propyl norbornene, 5,6-dicarboxy norbornene, The norbornene which has a polar group containing oxygen atoms, such as 5-carbomethoxy-6-carboxy norbornene; norbornene; etc. which have a polar group containing nitrogen atoms, such as 5-cyano norbornene and norbornene 5,6-imidodicarboxylate, are mentioned.

[0041] Especially, since crystallinity with high norbornene which has no replacing or a comparatively small substituent is shown, it is desirable. Specifically Norbornene, 5-methyl norbornene, 5-ethyl norbornene, 5-ethylidene norbornene, 5-vinyl norbornene, the norbornene 5,6-dicarboxylic anhydride, 5-hydroxymethyl norbornene, 5,6-JI (hydroxymethyl) norbornene, 5,5-JI (hydroxymethyl) norbornene, 5-cyano norbornene, and norbornene 5,6-imidodicarboxylate is mentioned.

[0042] As a norbornene derivative in which  $R^{38}$  and  $R^{41}$  join together and  $r$  of a general formula [10] has a ring structure by 0 in addition to a norbornene ring, the dicyclopentadienes whose ring structure is a five-membered ring, a norbornene derivative which has an aromatic ring, etc. can be mentioned. 4.3.1<sup>2</sup>, tricyclo [5.0] dec-3-ene which saturated a double bond of a five-membered

ring portion of a dicyclopentadiene or a dicyclopentadiene as an example of dicyclopentadienes, Tricyclo [4.4.1<sup>2,5</sup>.0] \*\*\*\*\*- 3-ene etc. can be mentioned. As a norbornene derivative which has an aromatic ring, Tetracyclo [6.5.1<sup>2,5</sup>.0<sup>1,6</sup>.0<sup>8,13</sup>] trideca- 3,8,10,12-tetraene (it is also called a 1,4-methano-1,4,4 a,9a-tetrahydro fluorene), Tetracyclo [6.6.1<sup>2,5</sup>.0<sup>1,6</sup>.0<sup>8,13</sup>] tetradeca- 3,8,10,12-tetraene (it is also called the 1,4-methano- 1, 4, 4a, 5, and 10 and 10a-hexahydroanthracene) etc. can be mentioned. Since the dicyclopentadienes shown by the above-mentioned example and a norbornene derivative which has an aromatic ring comprise only a ring structure, although a crystalline ring-opening-polymerization object or its hydride is obtained, it is preferred.

[0043]r of a general formula [10] as an example of tetracyclododecene which is 1, Tetracyclo dodecen, 8-methyltetracyclo dodecen, 8-ethyltetracyclo dodecen, Tetracyclododecene;8-methylidene tetracyclo dodecen which has no replacing or alkyl groups, such as 8-cyclohexyl tetracyclo dodecen and 8-cyclopentyl tetracyclo dodecen, 8-ethylidene tetracyclo dodecen, 8-vinyl tetracyclo dodecen, 8-propenyl tetracyclo dodecen, 8-cyclohexenyl tetracyclo dodecen, Tetracyclododecene which has aromatic rings, such as tetracyclododecene;8-phenyl tetracyclo dodecen which has a double bond in exocyclic [, such as 8-cyclopentenyl tetracyclo dodecen, ]; 8-carbomethoxy tetracyclo dodecen, 8-methyl-8-carbomethoxy tetracyclo dodecen, 8-hydroxymethyl tetracyclo dodecen, Tetracyclododecene which has a substituent containing oxygen atoms, such as 8-carboxy tetracyclo dodecen and tetracyclo dodecen 8,9-dicarboxylic acid, the tetracyclo dodecen 8, and 9-dicarboxylic anhydride;

[0044]8-cyano tetracyclo dodecen, The tetracyclo dodecen 8, Nitrogen atoms, such as 9-imidodicarboxylate. An included substituent. Tetracyclododecene which has a substituent containing halogen atoms, such as tetracyclododecene;8-chloro tetracyclo dodecen which it has; tetracyclododecene; etc. which have a substituent containing silicon atoms, such as 8-trimethoxysilyl tetracyclo dodecen, are mentioned. Especially, since crystallinity with high tetracyclododecene which has no replacing or a comparatively small substituent is shown, it is desirable. Tetracyclo dodecen, 8-methyltetracyclo dodecen, 8-ethyltetracyclo dodecen, 8-methylidene tetracyclo dodecen, 8-ethylidene tetracyclo dodecen, 8-vinyl tetracyclo dodecen, 8-hydroxymethyl tetracyclo dodecen, Tetracyclo dodecen 8,9-dicarboxylic anhydride, 8-cyano tetracyclo dodecen, and tetracyclo dodecen 8,9-imidodicarboxylate, 8-chloro tetracyclo dodecen, etc. are mentioned.

[0045]r of a general formula [10] as an example of the hexacycloheptadecen which is 2, Hexacycloheptadecen, 12-methylhexacycloheptadecen, 12-ethyl hexacycloheptadecen, 12-cyclohexyl hexacycloheptadecen, The hexacycloheptadecen which has no replacing or alkyl groups, such as 12-cyclopentyl hexacycloheptadecen; 12-methylidene hexacycloheptadecen, 12-ethylidene hexacycloheptadecen, 12-vinyl hexacycloheptadecen, 12-propenyl hexacycloheptadecen, 12-cyclohexenyl hexacycloheptadecen, The hexacycloheptadecen which has a double bond in exocyclic [, such as 12-cyclopentenyl hexacycloheptadecen, ]; hexacycloheptadecen which has aromatic rings, such as 12-phenyl hexacycloheptadecen;

[0046]12-carbomethoxy hexacycloheptadecen, 12-methyl-12-carbomethoxy hexacycloheptadecen, 12-hydroxymethyl hexacycloheptadecen, 12-carboxy hexacycloheptadecen, Hexacycloheptadecen;12-cyano hexacycloheptadecen which has a substituent containing oxygen atoms, such as hexacycloheptadecen 12,13-dicarboxylic acid and a hexacycloheptadecen 12,13-dicarboxylic anhydride, The hexacycloheptadecen which has a substituent containing nitrogen atoms, such as hexacycloheptadecen 12,13-imidodicarboxylate; Hexacycloheptadecen; which has a substituent containing halogen atoms, such as 12-chloro hexacycloheptadecen. The hexacycloheptadecen which have a substituent containing silicon atoms, such as 12-trimethoxysilyl hexacycloheptadecen, is mentioned.

[0047]The body and an isomer of exo\*\* are contained in the above-mentioned monomer. Although a monomer used for this invention may be a mixture of these isomers, in order to improve crystallinity more, its one in an isomeric mixture where composition ratio of one of isomer ingredients is higher is preferred. What usually has one of isomers [ not less than 80% of ] not less than 70% is especially specifically preferred.

[0048]In this invention, copolymerization of the monomer of copolymerizable others other than a

norbornene system monomer may be carried out to a norbornene system monomer. As a monomer of copolymerizable others, cyclic olefin other than a norbornene system monomer can be mentioned. As cyclic olefin other than a norbornene system monomer, cyclic olefin or diolefins, these substitution products, or a derivative of a monocycle of  $C_4 - C_{20}$  is mentioned.

As an example of the cyclic olefin of a monocycle, or diolefins, Cyclobutene, cyclopentene, methylcyclopentene, a cyclohexene, A cyclic olefin system monomer of a monocycle indicated to JP,64-66216,A, such as a methylcyclohexene, cycloheptene, and cyclooctane, etc.;

Cyclohexadiene, An annular diolefin system monomer indicated to JP,7-258318,A, such as methylcyclohexadiene, cyclo-octadiene, methyl cyclo-octadiene, and phenyl cyclo-octadiene, etc. can be mentioned.

[0049]In this invention, although a non-solvent can also perform a polymerization reaction, when performing a hydrogenation reaction, polymerizing in an organic solvent is preferred after a polymerization. An organic solvent used by this invention will not be limited in particular, if a polymer and a polymer hydride dissolve or distribute on condition of predetermined and do not influence a polymerization and hydrogenation.

[0050]As an example of such an organic solvent, they are aliphatic hydrocarbon system solvents, such as pentane, hexane, and heptane.; Cyclopentane, Cyclohexane, a methylcyclohexane, dimethylcyclohexane, Trimethylcyclohexane, ethylcyclohexane, diethylcyclohexane, Decahydronaphthalene, bicycloheptane, tricyclodecane one, hexahydro indene cyclohexane, Alicycle fellows hydrocarbon system solvents, such as cyclooctane; Benzene, toluene, Aromatic hydrocarbon system solvents, such as xylene; Dichloromethane, chloroform, Halogen system aliphatic hydrocarbon system solvents, such as 1,2-dichloroethane; Chlorobenzene, Halogen system aromatic hydrocarbon system solvents, such as dichlorobenzene; Nitromethane, Nitrogen-containing hydrocarbon system solvents, such as nitrobenzene and acetonitrile; Ether system solvents, such as diethylether and a tetrahydrofuran; Aromatic ether system solvents, such as an anisole and phenetol, etc. can be used. Also in these solvents, an aromatic hydrocarbon system solvent, an aliphatic hydrocarbon system solvent, an alicycle fellows hydrocarbon system solvent, an ether system solvent, or an aromatic ether system solvent is preferred.

[0051](Polymerization method) a rate of a polymerization catalyst over a monomer in a method of this invention -- a mole ratio -- (the transition metal:monomer in a polymerization catalyst), and 1:100 to 1:2,000,000 -- desirable -- 1:200-1,000,000 -- it is 1:500-1:500, and 000 more preferably. If there are too many catalyst amounts, catalyst removal will become difficult, and if too small, sufficient polymerization activity may not be acquired. When polymerizing in a solvent, as for concentration of a monomer, 1 to 50 % of the weight is preferred, its 2 to 45 % of the weight is more preferred, and especially its 3 to 40 % of the weight is preferred. A subsequent hydrogenation reaction may become difficult [ when concentration of a monomer is 1 or less % of the weight, productivity is bad, when it is 50 % of the weight or more, solution viscosity after a polymerization is too high, and ].

[0052]A polymerization reaction is started by mixing a monomer and a polymerization catalyst. Polymerization temperature in particular is not restricted. Generally,  $-30^{\circ}C - 200^{\circ}C$  are  $0^{\circ}C - 180^{\circ}C$  preferably. Polymerization time can be suitably chosen so that it may become a desired molecular weight and polymerization conversion, and it is usually for [ 1 minute ] - 100 hours.

[0053]As a method of adjusting a molecular weight of a ring-opening-polymerization object acquired, it can carry out by carrying out adequate amount addition of a vinyl compound or the diene compound. Especially if a vinyl compound used for molecular weight adjustment is an organic compound which has a vinyl group, it will not be limited, but. Alpha olefins, such as 1-butene, 1-pentene, 1-hexene, and 1-octene; Styrene, Styrene, such as vinyltoluene; Ethyl vinyl ether, i-butylvinyl ether, ether [ , such as allyl glycidyl ether, ]; -- containing halogen vinyl compound [ , such as an allyl chloride, ]; -- nitrogen content vinyl compounds, such as an oxygen content vinyl compound, acrylamide, etc., such as allyl acetate, allyl alcohol, and glycidyl methacrylate, etc. can be mentioned. A diene compound 1,4-pentadiene, 1,4-hexadiene, 1,5-hexadiene, Nonconjugated diene, such as 1,6-heptadiene, 2-methyl-1,4-pentadiene, and 2,5-

dimethyl-1,5-hexadiene, Or conjugated dienes, such as 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene, can be mentioned. With a molecular weight to calculate, quantity of a vinyl compound or a diene compound to add can be arbitrarily chosen between 0.1-10-mol % to a monomer.

[0054](Hydrogenation reaction) Under existence of a hydrogenation catalyst, a hydrogenation reaction supplies hydrogen in the system of reaction, and is performed. If it is generally used when hydrogenating an olefin compound as a hydrogenation catalyst, it will be usable and will not be restricted in particular, but the following is mentioned, for example.

[0055]A catalyst system which consists of combination of a transition metal compound and an alkali metal compound as a homogeneous catalyst, For example, cobaltous acetate/triethylaluminum, nickel acetylacetonato / triisobutylaluminum, Combination of titanocene dichloride / n-butyl lithium, zirconocene dichloride / sec-butyl lithium, tetrabutoxy titanate / dimethylmagnesium, etc., etc. is mentioned. Noble metal complex catalysts, such as dichlorobis (triphenyl phosphine) palladium, a chloro hydride carbonyltris(triphenyl phosphine) ruthenium, and chlorotris(triphenyl phosphine) rhodium, can be mentioned.

[0056]As a heterogeneous catalyst, metal, such as nickel, palladium, platinum, rhodium, and a ruthenium, Or a solid catalyst which made carriers, such as carbon, silica, diatomite, alumina, and titanium oxide, support these metal, For example, a catalyst system of nickel/silica, nickel/diatomite, nickel/alumina, palladium/carbon, palladium/silica, palladium/diatomite, palladium/alumina, etc., etc. is mentioned.

[0057]A hydrogenation reaction is usually performed in an inert organic solvent. As such an inert organic solvent, aromatic hydrocarbon system solvent; n-pentane, such as benzene and toluene, Aliphatic hydrocarbon system solvents, such as n-hexane; ether system solvent;, such as alicycle fellows hydrocarbon system solvent; tetrahydrofurans, such as cyclohexane and a decalin, and ethyleneglycol dimethyl ether, is mentioned. An inert organic solvent may be the same as a polymerization reaction solvent. In that case, a hydrogenation catalyst is made to add and react to polymerization reaction liquid as it is.

[0058]Although a hydrogenation reaction differs in a condition range for which it is suitable also by a hydrogenation catalyst system to be used, hydrogenation temperature -- usually -- it being 0-200 \*\* more preferably, and preferably, hydrogen pressure -10-220 \*\* -20-250 \*\*, usually, 0.1 - 50 kgf/cm<sup>2</sup> -- desirable -- 0.5 - 40 kgf/cm<sup>2</sup> -- it is 1.0 - 30 kgf/cm<sup>2</sup> more preferably. If too high [ when hydrogenation temperature is too low, reaction velocity is slow, and ], a side reaction will occur. If hydrogen pressure is too low, hydrogenation speed will become slow, and when too high, a high-withstand-pressure reaction apparatus is needed.

[0059]A hydrogenation rate is usually not less than 90% especially preferably not less than 80% more preferably not less than 70% not less than 50%, and hydrogenation reaction time can attain the above-mentioned hydrogenation rate in 0.1 to 10 hours.

[0060](A crystalline norbornene system ring-opening-polymerization object and a crystalline norbornene system ring-opening-polymerization object hydride) A crystalline norbornene system ring-opening-polymerization object and this ring-opening-polymerization object hydride are obtained as directed under this invention. This crystalline norbornene system ring-opening-polymerization object and this ring-opening-polymerization object hydride have the melting point. The melting point is usually in the range of 100-400 \*\*.

[0061]

[Example]An example and a comparative example are given to below, and this invention is explained to it still more concretely.

(1) The molecular weight of the ring breakage (\*\*) polymer was measured as a polystyrene reduced property by the gel permeation chromatography (GPC) which uses chloroform as a solvent.

(2) The hydrogenation rate was measured by the infrared absorption spectrum.

(3) With the differential scanning calorimeter, by a part for 10 \*\*/, temperature up of the melting point (Tm) and the glass transition temperature (Tg) was carried out, and they were measured.

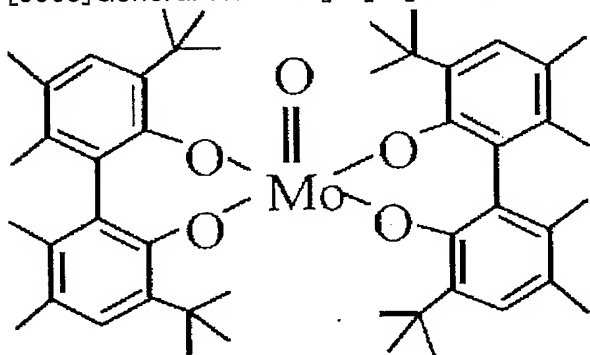
[0062](Example 1) To the glass reactor with an agitator, 1.5 copies of oxymolybdenum

tetrachloride ( $\text{MoOCl}_4$ ) and 30 copies of diethylether were added, and this was cooled to it at  $-78^\circ\text{C}$ . The solution which made 30 copies of diethylether dissolve 4.19 copies of 3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy lithium in a pan was added. This mixture was gradually returned to the room temperature, and the reaction was performed for 18 hours. reduced-pressure-drying  $^\circ\text{C}$  The  $^\circ\text{C}$  exception carried out the sediment with cerite after the reaction, and the solution portion was carried out. The solid A was obtained by cooling and settling this on  $-30^\circ\text{C}$ . The yield of the obtained solid was 2.56 copies. The  $^1\text{H-NMR}$  spectrum of this solid A was as follows.

$^1\text{H-NMR}(\text{benzene-d}_6)$   $\delta$  7.24 (s, 1,  $\text{H}_{\text{aryl}}$ ), 7.19 (s, 1,  $\text{H}_{\text{aryl}}$ ), 2.13 (s, 3,  $\text{CH}_3$ ), 2.03 (s, 3,  $\text{CH}_3$ ), 1.68 (s, 3,  $\text{CH}_3$ ), 1.67 (s, 3,  $\text{CH}_3$ ), 1.52 (s, 9, t-Bu), 1.45 (s, 9, t-Bu).

The result of the ultimate analysis of this solid A was as follows. Molybdenum 10.9 (wt%), carbon 70.6 (wt%), hydrogen 8.6 (wt%), chlorine  $<0.1$  (wt%), other 9.9 (wt%). In addition, 9.9 (wt%) is considered to be contribution of the oxygen which was impossible for measurement. such elementary composition — the elementary composition (molybdenum 11.7 (wt%).) of screw [3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy] oxymolybdenum (VI) Carbon 70.6 (wt%), hydrogen 7.9 (wt%), oxygen It was well in agreement with 9.8 (wt%). The reason of a gap of a theoretical value and measured value is considered to be contribution of extant diethylether. From the above result, it is presumed that the structure of the solid A is screw [3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenoxy] oxymolybdenum (VI) (general formula [11]).

[0063]General formula [11] : [Formula 11]



[0064](Example 2) After adding the solid A 0.092 copy and four copies of toluene which were compounded in Example 1 to the glass reactor with an agitator, this was cooled at  $-78^\circ\text{C}$ . What furthermore dissolved 0.0145 copy of n-butyl lithium in one copy of hexane was added, this was returned to the room temperature, and the reaction was performed for 1 hour. 7.5 copies of dicyclopentadienes (DCPD), 27 copies of toluene, and 0.1 copy of 1-hexene were added into the obtained mixture, and the polymerization reaction was performed into it in  $80^\circ\text{C}$ . The promptly white sediment deposited after the polymerization reaction start. Filled polymerization reaction liquid with a lot of methanol, the sediment was made to condense after a 2-hour reaction, and reduced pressure drying was carried out at  $40^\circ\text{C}$  after [classified by  $^\circ\text{C}$ ] washing for 24 hours. The yield of the acquired ring-opening-polymerization object was 7.4 copies, and the number average molecular weight ( $M_n$ ) was [8,000 and weight average molecular weight ( $M_w$ ) of the molecular weight (polystyrene conversion)] 15,000. The melting point ( $T_m$ ) was  $245^\circ\text{C}$ .

[0065](Example 3) 3.0 copies of ring-opening-polymerization objects and 47 copies of cyclohexane which were obtained in Example 2 were added to autoclave with an agitator. Subsequently, what dissolved 0.0187 copy of bis(tri-cyclohexyl phosphine)benzylidyne ruthenium (IV) dichloride and 0.45 copy of ethyl vinyl ether in ten copies of cyclohexane is added to the above-mentioned autoclave, The hydrogenation reaction was performed at hydrogen pressure  $8\text{ kgf/cm}^2$  and  $175^\circ\text{C}$  for 8 hours. What filled a lot of isopropanols with this reaction mixture, and generated it was thoroughly deposited after the hydrogenation reaction, and reduced pressure drying was carried out at  $40^\circ\text{C}$  after [classified by  $^\circ\text{C}$ ] washing for 24 hours. The hydrogenation rate of the obtained ring-opening-polymerization object hydride was not less than 99% from the



result of the infrared absorption spectrum. T<sub>m</sub> was 275 °C.

[0066](Example 4) To the glass reactor with an agitator, 0.425 copy of 3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenol (BMBP), five copies of toluene, and five copies of tetrahydrofurans (THF) were added, and this was cooled to it at -78 °C. What dissolved 0.231 copy of n-butyl lithium in 1.5 copies of n-hexane was added, it returned to the room temperature gradually, and the reaction solution A was obtained. To the glass reactor with an agitator different from the above, 0.152 copy, ten copies of toluene, and ten copies of tetrahydrofurans were added for oxymolybdenum tetrachloride (MoOCl<sub>4</sub>), and this was cooled to it at -78 °C. The above-mentioned reaction solution A whole quantity was added in this solution, and this mixture was gradually returned to the room temperature. After returning to a room temperature, it stirred for 30 minutes at 50 °C. This solution was cooled at -78 °C, what dissolved 0.151 copy of n-butyl lithium in this solution at 0.75 copy of n-hexane was added, it returned to the room temperature gradually, and the catalyst solution B was obtained. The catalyst solution B was added to the glass reactor with an agitator which added 24 copies of dicyclopentadienes, 96 copies of toluene, and 0.3 copy of 1-hexene, and the polymerization reaction was performed in 80 °C for 2 hours. The promptly white sediment deposited after the polymerization reaction start. The obtained polymerization reaction liquid was filled with a lot of methanol, and the sediment was made to condense. Reduced pressure drying of the reaction mixture containing this sediment was carried out at 40 °C after [classified by °C] washing for 24 hours. The yield of the acquired ring-opening-polymerization object was 23.5 copies, and T<sub>m</sub> was 245 °C.

[0067](Example 5) Catalyst preparation and a polymerization reaction were performed like Example 4 except having replaced with oxymolybdenum tetrachloride and having used tungsten hexachloride. The yield of the acquired ring-opening-polymerization object was 23.5 copies, and T<sub>m</sub> was 245 °C.

[0068](Example 6) Catalyst preparation and a polymerization reaction were performed like Example 4 except having replaced with oxymolybdenum tetrachloride and having used dioxydichloromolybdenum. The yield of the acquired ring-opening-polymerization object was 15.6 copies, and T<sub>m</sub> was 245 °C.

[0069](Example 7) Catalyst preparation and a polymerization reaction were performed like Example 7 except having replaced with the dicyclopentadiene and having used norbornene (NBE). The yield of the acquired ring-opening-polymerization object was 23.5 copies, and T<sub>m</sub> was 105 °C.

[0070](Example 8) Three copies of ring-opening-polymerization objects and 47 copies of cyclohexane which were obtained in Example 4 were added to autoclave with an agitator. Subsequently, the hydrogenation catalyst solution which dissolved 0.04 copy of nickel acetate and 0.18 copy of triisobutylaluminum in ten copies of cyclohexane was added, and the hydrogenation reaction was performed at hydrogen pressure 10 kgf/cm<sup>2</sup> and 160 °C for 8 hours. A lot of isopropanols were filled with this hydrogenation reaction liquid, polymer was deposited thoroughly, and reduced pressure drying was carried out at 40 °C after [classified by °C] washing for 24 hours. The hydrogenation rate of the obtained ring-opening-polymerization object hydride was not less than 99% from the result of the infrared absorption spectrum. T<sub>m</sub> was 275 °C.

[0071](Examples 9-11) The hydrogenation reaction was performed like Example 8 using the polymer obtained in Examples 5-8. A result is shown in Table 1.

[0072](Example 12) Catalyst preparation and a polymerization reaction are performed like Example 4 except having replaced with 3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenol, and having used 2,6-JI (t-butyl)-4-methyl phenol (BHT), And the hydrogenation reaction was performed like Example 8. A result is shown in Table 1.

[0073](Comparative example 1) Catalyst preparation and a polymerization reaction were performed like Example 1 except having replaced with 3,3'-JI (t-butyl)-5,5',6,6'-tetramethyl 2,2'-biphenol, and having used phenol. The reaction solution was still uniform after the end of a polymerization reaction. T<sub>m</sub> was not observed although glass transition temperature (T<sub>g</sub>) was observed near 125 °C.



[0074](Comparative example 2) The hydrogenation reaction was performed like Example 8 using the polymer obtained by the comparative example 1. The reaction solution was still uniform after the end of a hydrogenation reaction. T<sub>m</sub> was not observed although T<sub>g</sub> was observed near 95 \*\*.

[0075]

[Table 1]

		金属ハロゲン 化合物	フェノール類	モノマー	T <sub>m</sub> (°C)			T <sub>m</sub> (°C)
実施例	4	MoOCl <sub>4</sub>	BMBP	DCPD	245	実施例	8	275
	5	WCl <sub>6</sub>	I	I	225		9	280
	6	MoO <sub>2</sub> Cl <sub>2</sub>	I	I	245		10	281
	7	MoOCl <sub>4</sub>	I	NBE	105		11	146
	12	MoOCl <sub>4</sub>	BIT	DCPD	263			
比較例	1	MoOCl <sub>4</sub>	フェノール	DCPD	観測されず	比較例	2	観測されず

[0076]As mentioned above, by according to an example and the comparative example, carrying out ring opening polymerization of the norbornene system monomer using the polymerization catalyst which consists of reactant (III), or compound (IV) and organic metal reducing agent (II), and hydrogenating if needed, Have the melting point, i.e., the polymer or hydride which has crystallinity carries out ring opening polymerization of the norbornene system monomer using the polymerization catalyst which consists of reactant (I) obtained with high yield, and organic metal reducing agent (II), and by hydrogenating, That is [ it has the melting point ], it turns out that the polymer or hydride which has crystallinity is obtained with high yield.

[0077]

[Effect of the Invention]According to this invention, the manufacturing method of the crystalline norbornene system ring-opening-polymerization object which uses the polymerization catalyst which gives a crystalline norbornene system ring-opening-polymerization object and a crystalline norbornene system ring-opening-polymerization object hydride, and this polymerization catalyst, and this ring-opening-polymerization object hydride is provided.

[Translation done.]